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DATA REDUCTION FOR A HIGH-THROUGHPUT
NEUTRON ACTIVATION ANALYSIS SYSTEM

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by

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ABSTRACT

To analyze samples collected as part of a geochemical survey for the National Uranium Resource Evaluation Program, Savannah River Laboratory has installed a high-throughput neutron activation analysis system. As part of that system, computer programs were developed to reduce raw data to elemental concentrations in two steps. Program RAGS reduces gamma ray spectra to lists of photopeak energies, peak areas, and statistical errors. Program RICHES determines the elemental concentrations from photopeak and delayed neutron data, detector efficiencies, analysis parameters (neutron flux and activation, decay and counting times) and spectrometric and cross section data from libraries. Both programs have been streamlined for online operation using a minicomputer, each requiring ~64 kbyte of core.

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INTRODUCTION

The National Uranium Resource Evaluation (NURE) program is being conducted by the Grand Junction Office of the U.S. Department of Energy to survey the continental United States for potential uranium-bearing districts. The Savannah River Laboratory (SRL) has the responsibility for a geochemical reconnaissance¹ of 2.2 million km² in 30 eastern states. Approximately 300,000 samples of stream sediment and ground and surface water are being collected and analyzed for U, Th, and associated elements. Neutron activation analysis was chosen as the prime analytical technique, because of its sensitivity and specificity for uranium, especially when beta-delayed neutron counting is combined with recycle analysis regimes. SRL constructed a pilot-scale activation facility which processed 20,000 samples. That facility has been expanded to increase capacity to at least 100,000 samples per year.

Typical analysis regimes are summarized in Table 1 for 0.5 to 1.5-g sediment samples and for 5-g ion-exchange resin samples which contain the ions concentrated from 1L of filtered ground or surface water. The raw data acquired for a typical sample include: 1 to 3 gamma ray spectra, delayed-neutron counts, timing information for each analysis step, neutron flux monitor readings, and codes describing the detectors and counting geometries.

With the pilot facility, the raw data were recorded on magnetic tape for offline reduction using a series of batch programs written for our IBM 360-195 computer. With the expanded facility, the data are reduced online using an SEL 32-55 computer. With both

software systems the raw data and elemental composition of each sample are routed to the IBM 360-195 computer for archival storage and inclusion in the NURE data management system.² The programs described below are common to both systems with relatively minor differences in communication linkages between steps.

METHOD

Data reduction in the upgraded facility is a two-step process: 1) Each gamma ray spectrum is reduced immediately upon acquisition to a list of photopeak energies, peak areas, and statistical errors using a module called RAGS. 2) After the last analysis step is completed for a sample and the corresponding spectrum reduced by RAGS, program RICHES is activated to determine the elemental composition of the sample using the data acquired from all activation regime steps.

Program RAGS

The basic logic of the spectrum reduction program RAGS has been detailed elsewhere.³ Briefly, the spectrum is smoothed, peak boundaries are located by following the sign of the smoothed first derivative, peak areas are determined by simple summations between boundaries with correction for overlapping peaks, and peak center is located from the maximum of a least-squares quadratic fit of channels above half maximum.

To assign a photopeak to an element, it is necessary to have a reasonably accurate conversion of peak center to peak energy. This is a multistep procedure in RAGS as follows:

- 1) Rough energies are approximated from channel-vs.-energy calibration data stored on disk for the appropriate detector on the day the data were acquired.
- 2) The rough energies are matched within liberal windows to a list of prominent photopeaks normally acquired in the spectrum. A linear least-squares fit of the matched photopeaks yields better values for the energies.

3) Matching process is repeated with smaller windows. A cubic least squares fit produces the final energies for the spectrum.

The list of photopeak energies, peak areas, and statistical errors generated by RAGS is stored in random-access disk files for later use by program RICHES.

Program RICHES

If all of the samples were essentially equivalent in composition and were processed under identical activation regimes, the conversion of photopeak areas to elemental concentration would be a straightforward computation. However, elemental concentrations vary by orders of magnitude, the details of the activation regimes are not constant, and equipment malfunctions may preclude acquisition of some data. Because we are working in a production environment, our philosophy is to acquire as much data as economically feasible for each sample and then screen the data so that the best possible results are reported for each element in each sample. Program RICHES was designed to sort through all data acquired for a sample and to convert to elemental concentration only those data successfully screened.

The algorithm used in RICHES is to set up and solve (by a nonlinear least-squares method) the following set of equations:

$$P_j = \sum_i a_i R_{ij} \quad (1)$$

where P_j = area of photopeak j

a_i = μg of element i in the sample

R_{ij} = photopeak area for j if 1 μ g of element i were present in the sample.

The calculation of R_{ij} is made from the spectrometric and cross section library data compiled for each activation product isotope, detector efficiency calibrations, and the analysis history (neutron flux and the activation, decay and counting times) of the sample.

Ideally we would obtain as many Equation (1)'s as there are photopeaks; each element would contribute a term if it had a transition which matched the photopeak in energy. With real data, however, a finite energy window must be used to accommodate variations between the tabulated transition and experimental photopeak energies. To minimize the number of mismatched elements and maximize the quality of the results, the search for energy matches is limited to isotope/spectrum combinations for each element which have the highest probability of yielding valid results.

In a program RICHES the order and extent of the search for energy matches is determined by the following steps for each element:

- 1) A "detection limit" is calculated for each product isotope in each spectrum using R_{ij} calculated for the most-abundant transition of the isotope and a minimum detectable photopeak area at the appropriate energy (obtained by interpolation of statistical errors of photopeaks neighboring in energy). For an element with 4 gamma-active product isotopes and an analysis regime yielding 3 gamma spectra, twelve "detection limits" would be calculated.

The isotope/spectrum combinations are arranged in ascending order of "detection limit," the smallest value of which becomes the reported detection limit for the element in the sample.

- 2) The search for transition/photopeak energy matches begins with most sensitive isotope/spectrum combination (lowest "detection limit"). The spectrometric data are arranged in the library in descending order of transition abundance. Values of R_{ij} are added to the array corresponding to Equation (1) only if the transition and photopeak energies agree within narrow limits. The search is terminated for a combination if an energy match is not found for a transition where abundance is less than one fifth the abundance of the last matched transition. The search continues for an element with the next most-sensitive combination; search terminates when a combination fails to yield any matches.
- 3) Each of the equations obtained in Step (2) is weighted by a factor containing the statistical error of the photopeak and the relative effectiveness of each element's contribution to the photopeak area. The weighting process effectively minimizes the contribution of multiply matched photopeaks on the concentration values calculated by the least-squares routine. The relative effectiveness of an element's contribution is estimated from the detection limit of the element divided by the combination's "detection limit."

After all elements in the data library have been searched for energy matches, only the equations obtained in Step (2) having at least one nonzero value for R_{ij} are input to the non-linear least-squares routine to return values for concentrations (a_i) and statistical errors in concentration for matched elements.

For ease of discussion the steps described above apply to the processing of gamma ray data only. The beta-delayed neutron data are processed in the same manner by setting the "photopeak" and "transition energies" to 10 MeV for delayed neutrons. R_{ij} 's for oxygen and thorium are included in the delayed-neutron equations only if the gamma-active products for these elements are also matched.

The results reported for a sample are the concentration values and errors for matched elements and the detection limit for unmatched elements.

Table 2 summarizes the computer resources required for the IBM 360-195 pilot version and the SEL 32-55 production versions of these programs. The restructuring of the programs for installation on the SEL 32-55 control computer significantly reduced the core requirements and execution speed (the IBM 360-195 is inherently faster by a factor of ~4),

DISCUSSION

Approximately 20,000 samples were processed in the pilot facility; the production facility became operational only recently. The results summarized in Table 3 are from the pilot facility for a sample used as a system monitor. An aliquot of monitor was routinely substituted for every 25th sample over a 9-month period. Unfortunately the sample was >90% SiO₂ with relatively low concentrations for minor and trace elements, many of which are near or below the detection limit. With typical sediment samples, the probability of detecting an individual element is much higher than indicated in Table 3. The accuracy of the results as indicated by analyses of USGS reference material is generally within 10% if the element is significantly above the detection limit.

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TABLE I
Typical Analysis Regimes

Sample Type	Regime Step	No. of Cycles	Time, sec			No. of Spectra Acquired
			Activation	Decay	Count	
Sediment ^a	1	1	2	1.5	2	-
	2	20	6	1.5	6	1
	3	1	900	600	600	1
	4	1	-	10-14 days	1000	1
Resin ^b	1	1	2	1.5	2	-
	2	20	6	1.5	6	1

a. 0.5 to 1.5 g of stream sediment.

b. 4.5 g of ion exchange resin on which 1 liter of water was concentrated.

TABLE II
Computer Resources Required for Reduction Programs

	Core, kbytes	CPU(s)	Elapsed(s)
RAGS			
Pilot	300	0.5/spectrum	2/spectrum
Production	63	1.7/spectrum	3/spectrum
RICHES			
Pilot	497	3/sample	10/sample
Production	66	6/sample	12/sample

TABLE III
Precision of Sample SRL 2.1 Analyses

Element	Number ^a	Mean, ppm	Standard Deviation, $\pm 1 \sigma$	Coefficient of Variation, %
U	269	7.80	0.27	3.4 ^b
Th	259	25.8	4.8	18.7 ^c
Hf	269	69.4	4.4	6.4 ^b
Ce	256	130	31	23.7 ^c
Dy	268	11.3	2.8	24.8 ^b
Ti	256	8890	1580	17.8 ^c
V	256	35.4	5.9	16.7 ^c
Fe	221	5550	2030	36.6 ^c
Mn	250	166	37	22.0 ^c
Al	256	20200	2150	10.6 ^b
Sc	269	3.50	0.88	25.2 ^c
La	244	79.4	18.6	23.5 ^c
Sm	234	10.5	3.7	34.9 ^c
Eu	123	1.45	0.92	63.3 ^c
Yb	242	10.0	3.6	35.5 ^b
Lu	234	2.87	0.93	32.3 ^c

- a. Number of determinations reported for 269 aliquots.
- b. Precision is probably about the same for samples as for SRL 2.1 standard.
- c. Precision is probably better for samples, because their concentrations are higher than those of SRL 2.1.